OPTIMIZATION IN THE TREATMENT OF SPENT POT LINING AND ENRICHING OF ITS CARBON PERCENTAGE BY HYDROCHLORIC ACID LEACHING

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Sidhant Chand

Roll no. 111CH0065

Under the supervision of

Prof. Pradip Rath

DEPARTMENT OF CHEMICAL ENGINEERING,

NATIONAL INSTITUTE OF TECHNOLOGY

ROURKELA, ODISHA

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National Institute of Technology, Rourkela

Department of Chemical Engineering

CERTIFICATE

This is certified that the work contained in the thesis entitled "Optimization in the Treatment of Spent Pot Lining and Enriching of its Carbon Percentage by Hydrochloric Acid Leaching" submitted by Sidhant Chand (111CH0065), has been carried out under my guidance and supervision and this work has not been submitted elsewhere for a degree.

Date: _____

Place: Rourkela

Prof. Pradip Rath
(Thesis Supervisor)
Professor& HOD,
Department of Chemical Engineering
NIT Rourkela-769008

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Date: _____

Sidhant Chand
111CH0065

ABSTRACT

Due to a rise in demand of aluminium, the undesirable production of Spent Pot Lining in the Hall-Heroult process has been increasing side-by-side, owing to added environmental problems. The aim of this project is to optimize the process parameters so as to enrich maximum amount of graphitic carbon from Spent Pot Lining, by using sodium hydroxide followed by hydrochloric acid for the first time. The Taguchi method approach for optimization was adopted and significant process parameters such as temperature, alkali concentration, acid concentration and L/S ratio were optimized. Characterization of the various SPL samples was also done to qualify and quantify the samples, using XRD, SEM-EDX, FESEM-EDX, CHNS analysis. The carbon percentage of SPL was increased from 43.39% to 70.44% which was confirmed from the ultimate analysis. From EDX data analysis, the carbon percentage was increased from 33.27% to 86.78%. Alkali concentration contributed 47.27% in the leaching process among the four factors, while acid concentration contributed only 1.02 %. The maximum leaching percentage was found to be 54.11% from experimentation. Finally, the analysis of the leaching capacity of four acids, $HClO_4$, H_2SO_4, HNO_3 and HCl was done graphically and comparisons were made.

Key words: Spent pot liner, Taguchi method, chemical leaching, ultimate analysis.

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ABBREVIATIONS

Adj.SS: Adjusted Sum of Squares

Adj.MS: Adjusted Mean Squares

Al_2O_3: ALUMINA (Corundum)

$Al(OH)_3$: Gibbsite (Aluminium Hydroxide)

ANOVA: Analysis of Variance

C: CARBON

CaF_2: Fluorite (Calcium Fluoride)

CHNS: Carbon, Hydrogen, Nitrogen, Sulfur

DOE: Design of Experiment

EPA: Environmental Protection Agency

EDX: Energy-Dispersive X-ray Spectroscopy

FESEM: Field Emission Scanning Electron Microscope

L/S: Liquid to Solid

M: Molarity

Na_3AlF_6: Cryolite

$NaAl_{11}O_{17}$: Diaoyudaoite (Sodium Aluminium Oxide)

NaF: Villiaumite (Sodium Fluoride)

SEM: Scanning Electron Microscope

Seq. SS: Sequential Sum of Squares

SD: Standard Deviation

SPL: Spent Pot Lining

S/N Ratio: Signal to Noise Ratio

XRD: X-Ray Diffraction

1. INTRODUCTION

1.1 ALUMINIUM AND ITS PRODUCTION

Aluminium is known to be the third most abundant element (after oxygen and silicon), and in the earth crust, it is the most abundantly found metal. Making up about 8% by weight of the earth's surface, it is an extremely valuable metal and could be considered as one of the backbones of the country. Being highly chemically reactive, its native varieties are uncommon and restricted to highly reducing surroundings. As a substitute, it is found in a combined state in over 260 different natural resources or minerals. Bauxite is the main source for this metal. Over 90% of the world's bauxite resources are concerted in the tropical and sub-tropical belt in Surinam, Australia, India, Brazil, Guinea and Jamaica. Nepheline ore deposits native to Australia are located on the Kola Peninsula as well as in the Kemerovo area. The nepheline processing leads to the generation of significant volumes of by-products like, potash, calcined soda, cement and fertilizers

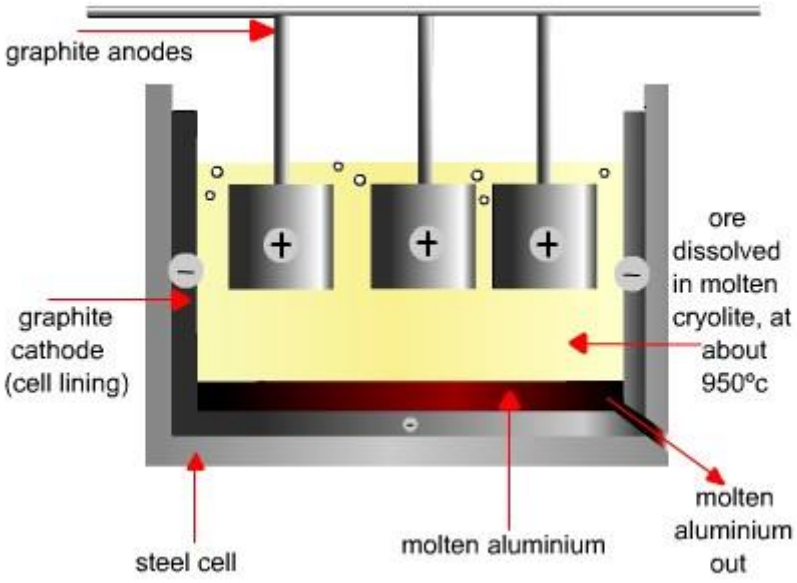
Alumina (Al_2O_3), is the basic raw material ore for aluminium production, which is a kind of extracted ore. An electrolytic redox reaction transforms alumina into aluminium. For every 1.95 tonnes of alumina, one tonne of aluminium is produced. The ore Bauxite comprises of 40-60% alumina, plus a hoard of other minerals like oxides of silicon, iron and titanium. The Bayer process is a chemical process used to first enrich pure alumina. It involves heating of the ore in an autoclave, with the addition of caustic soda. After cooling down, a solid residue is formed called "red mud", which is separated from the liquid. Calcination of aluminium hydroxide is done thereafter, post extraction from the solution.

1.2. HALL HEROULT PROCESS

Hall-Heroult process is an electrolytic reduction process where alumina is separated into its constituent components, i.e. aluminium metal and oxygen gas. Since alumina has a melting point on the higher side, it has to be dissolved in a cryolite bath material (Na_3AlF_6) in electrolytic cells which are also referred to as "pots", where oxidation of the coke anodes take place. For lowering the melting point, the cryolite-alumina mixture should also consist of numerous amounts of additional salts, like, calcium fluoride (CaF_2), aluminium fluoride (AlF_3), lithium carbonate (Li_2CO_3) and seldom, magnesium fluoride (MgF_2) as well, to further reduce the melting point for easy operation, improvement in current efficiency as well as to reduce the

losses due to evaporation. For every tonne of aluminium production, the smelting process consumes about 2 tonnes of alumina, 0.5 tonnes of anode coke, and slight amounts of fluoride salts, in addition to electrical power.

For a heavy resistance to the channel of a big electric current, the cryolite bath is kept in a molten state and the temperatures are maintained at around 920°- 980°C. The aluminium metal is separated by electrolysis reaction (as given below) and needs to be frequently removed for consequent casting. The pots are linked in a series electrically to form what is known as a 'potline.' In each pot, a direct current passes from graphite anodes, through the cryolite+salt bath containing alumina in solution, to the carbon cathode cell lining, and further to the anodes of the next pot and so on. Steel bars fixed in the cathode of the cell carry the current out of the pot, whereas the pots themselves are a part of the linked aluminium bus-bar system. A steel shell is present in the pot where the carbon cathode lining is contained. This lining holds the molten cryolite+salts and alumina in solution state and the molten aluminium is created in the process.



Anode: (positive electrode)	$C_{(s)} + 2O^{2-}{}_{(l)}$	→	$CO_{2(g)} + 4e$
Cathode: (negative electrode)	$Al^{3+}{}_{(l)} + 3e$	→	$Al_{(l)}$
Overall Reaction:	$2Al_2O_{3(l)} + 3C_{(s)}$	→	$4Al_{(l)} + 3CO_{2(g)}$

Figure 1.1: Representation of Hall-Heroult cell and reactions involved inside the cell.

An electrically insulated edifice attached above the shell stores alumina routinely transported via a sealed system, and clasps the carbon anodes, appending them in the pot. The electrolyte consisting of molten cryolite comprising of dissolved alumina filling the space between the anodes in the pot, forms a dense coating at the surface of the electrolyte. The coating is broken sporadically and alumina is moved into the electrolyte to maintain concentration. With the progress of the electrolytic reaction aluminium, being somewhat denser than the pot bath material, it is constantly dumped in a metal pool on the bottommost point of the pot while oxygen reacts with the carbon of the coke anodes to form carbon dioxide. As the anodes are expended during the process, they must be unremittingly dropped to maintain a continuous distance between the anode and the exterior of the metal, being electrically a part of the cathode. The anodes are substituted on a steady outline. The energetic evolution of carbon dioxide at the anode mixes the added alumina into the electrolyte, but with it carries off any other volatile materials (including some fine solids).

Roughly 13 -16 kilowatt-hours of DC electrical energy, 1.5 kg of carbon, and 2 kg of aluminium oxide are consumed per kilo of aluminium produced. As electrolysis progresses, the aluminium oxide content of the bath is reduced and is recurrently restocked by feed additions from the pot's alumina storage to uphold the dissolved oxide content at about 3 to 5 percent. The occurrence of anode effect may occur if the alumina concentration decreases to about 1.5 to 2 percent. If anode effect occurs, the wetting of the carbon anode ceases, plus a gas film is formed under and about the anode. A high electrical resistance is caused and the normal pot voltage increases to about 10 to 15 times the normal level. Alteration is obtained by computer controlled or manual techniques resulting in amplified alumina content of the bath. The melted electrolyte bath consists mainly of cryolite (sodium aluminium fluoride) plus some aluminium fluoride, 6-10 percent by weight of fluorspar and 2-5 percent aluminium oxide.

1.3.CATHODES AND ANODES

The carbon lining on the pot cavity contains carbon blocks, pre-formed by outlying producers. These are placed in the steel pot shell and flagged together with a paste similar to that used in making the blocks. Large steel bars, aiding as electrical current amassers, are entrenched in the end portion of the hollow lining and outspread through overtures in the casing to link with the electrical bus which connects one pot to the next. Thermal padding consisting of vermiculite or similar refractory materials occupies the place between the cavity lining and the steel shell.

Carbon pot linings are designed to normally last 4 to 6 years. When failure of a lining occurs, essentially due the reaction of aluminium metal with the cathode collectors and numerous slow kinetic side reactions, the collectors tend to dissolve. Then, the metal and cryolite bath have a seepage around the collectors. An unexpected increase in iron levels in the aluminium is the best indicator that a pot is approaching the end of its service life. The lining has to be revamped at the point(s) of failure by a technique called "patching", or else the entire lining and collector muster has to be replaced. The second procedure is called "relining". Both pot patching and relining are a noteworthy part of the manufacture outflow.

1.4.SPENT POT LINERS

During service, molten cryolite slowly gets reduced and the sodium fluoride crystal deposits within the fine crevices of pot liner creating defect spots. As time passes, these crystals grow and exert pressure within these cracks resulting in the propagation of crack. As a consequence, with time the pot liner loses its electrical property and ultimately being discarded. These rejected waste pot liners are called “spent pot liners” (in short SPL). Spent Pot Liners are not only polluted by fluoride but also by other toxic elements such as cyanides (formed at high temperature reaction with atmospheric nitrogen), alkalis and aluminium. Table-1 below shows typical range of the contaminants in such cast-off pot liners along with concentration of these toxic elements in SPL carbon powder after refinement with oxidizing acids.

Table- 1.1: Typical contaminants in SPL and their concentration after chemical treatment with oxidizing acids.

Contaminants in untreated SPL	*Contaminants in treated SPL*
Fluoride - 6-9%	Fluoride 140-170 ppm
Aluminum - 1-2%	Aluminum 10-15 ppm
Cyanide - 0.2-0.4%	Cyanide 0.1 to 0.2 ppm
Alkali - 7-9%	Alkali 0.5-0.7%

In practice suitability of a specific component in a commercial recipe is tested by evaluating some gross property of the modified recipe against the production recipe of the compound. For example, in development of foundry chemicals (like mould coating, tundish cover, hot tops etc.) which basically is a blend of various components in a formulation, various substitutes are being tried with above procedure of gross estimation of certain properties of the compound in

order to determine its suitability. Similarly in present case of developing suitable substitute of carbonaceous material in commercial tap hole compound recipe, following properties are important in order to determine its appropriateness:

Apparent porosity: This property determines the ease with which gas generated in the tap hole compound during carbonization can escape easily without breaking or decreasing strength of the carbonized tap hole mass. This value is generally sustained in the range 25-35%.

Bulk density: This is maintained in the range 1.3-1.6 gm/cc in all commercial recipe in order to match with standard pushing length required by the equipment to fill the tap hole.

Conversion of *by-product carbon* obtained from spent pot liner treatment plant of aluminium industries to blast furnace tap hole mass. This value is limited within the narrow range of 0-2.5% in order to guarantee adhesion of the tap hole compound to brick lining and also not to crumple during carbonization.

Cold crushing strength: This value is maintained over a broad range of 40-160 kg/cm^2 in order to allow the carbonized tap hole compound withstand metallostatic pressure in the furnace while it is soft enough to be drilled out after the campaign is over by standard equipment.

Because of the presence of these toxic elements in large quantities, disposal of spent pot liners in open field poses great environmental risk. Moreover, generation of these spent pot liners by aluminium smelter plants on regular basis being very high (NALCO, Angul itself produces 450 tonnes spent pot liners per month on the averages) safe disposal of such huge quantity of toxic waste material have been a long standing problem with all aluminium smelters round the world. Efforts have been made to decontaminant these SPL by hydrothermal treatment with partial success as only 45% of the contaminants gets washed out by this process. Concentrated alkalis while leaches away most of the contaminants, extent of removal of the contaminants is very low and cannot be translated into actual plant practices. Accordingly majority of smelters at present adopts a policy to crush these spent pot liners to fine powder and burn them in a PF-burner. While this process destroys contaminants in the SPL, it emits pollutant gases such as fluorides and not acceptable by present plant practices.

As mentioned earlier, preparation of pot liners comprises use of special carbons and recovery of these valuable carbons in terms of its real commercial value outweighs many times than realizing its calorific value alone. Spent pot liner on the other hand can be decontaminated by

treatment with various strong oxidizing acids. *IMMT, Bhubaneswar, India* scaled up such a wet process which extracts all the contaminants in SPL in liquid phase and simultaneously recovers its carbon value as a by-product. Accordingly the process while decontaminates SPL, generates by-product carbon powder which can be used to make a number of important industrial carbon products. Attempts have also been made to utilize the spent pot liner in producing cement from spent pot liner. In such case the spent pot liner is used as a fuel supplement as well as mineralizing agent in cement kiln. In present experiments the SPL derived carbon powder was used to prepare blast furnace tap hole mass an important industrial product which consumes large volume of semi-crystalline carbon. Another reason to find possible use of SPL carbon powder in above product was relative cost of the carbon powder obtained as by-product from SPL treatment plant.

Since the reduction of alumina occurs in a molten bath of cryolite at 930-1000°C, the carbon cathode lining becomes infused with several fluoride compounds and a little however notable of cyanide (principally from the reaction between nitrogen and carbon in the presence of sodium at high temperatures). In the long run the cell falls flat as the voltage builds or iron begins to be noticed in the aluminium metal. Toward the end of the operational lifetime of the cells, the linings are detached and disconnected and the shell must be relined. On the other hand, the spent lining material, which is made out of carbon, refractory material and cryolite, including fluorine, aluminium, sodium, calcium and silicon values, alongside free and complex cyanides, carbides and nitrides, is dangerous and must be treated with extraordinary alert. Likewise, it is leachable, and it can, in specific conditions, create a combustible and harmful gas. SPL likewise contains materials that are profitable if recovered and utilized for particular purposes. The principle segments with potential quality are carbon and fluorides[1].

The harmless removal of spent linings has for quite a while showed a test to the industry. With the given ecological regulations of Indian government, the test continues. The clearance deposits should have low concentrations of fluorides and cyanides. The current management framework includes disposal in securing landfill to avoid leakage of fluoride and cyanide. Central Pollution Control Board reports that the specific generation degree for spent pot lining in our nation varies from 43 to 62 Kg per ton of aluminium supplied which represents a generation of 90000 tons of SPL per year. The carbon portion typically contains 4-8% leachable fluoride as well as 0.01-0.025% leachable cyanide.

2. LITERATURE REVIEW:

2.1. SPENT POT LINING (SPL)

The electrolytic cell lining are fabricated in a steel shell. It comprises of carbon, silicon carbide (SiC) or carbon used in the sidewalls. The refractory bricks get lined below the carbon lining to provide mechanical support. During the electrolysis process the lining is subjected to highly reducing conditions and generally fails after 5-8 years of operation depending on the cell construction, design approach and operation[16,22].

Generally in Soderbergs produce of 35kg/tonne, end to end (EE) technology prebakes 20-28 kg SPL/tonne. Usually in prebake technology the lining lasts for about 2700-3000 days with amorphous carbon blocks, 2400 days with semigraphite blocks, and 1700-2200 days with graphitized or graphitic blocks. Typical lifetime of Soderbergs is of 2500-2700 days with amorphous blocks and 3000 days if graphitized blocks are used. These data are known by the amount of aluminium produced per unit area (a reckoner of the volume of cell material). The amount of aluminium is not continual throughout the time period due to rise in voltage in cell systems. A careful observation is required in defining the production of SPL per tonne of aluminium produced[9, 13, 22].

The failure of cell linings leads to the spent cathode linings, which are usually discarded. The final waste product, called “Spent Pot Lining” is generated. Both first cut and second cut materials are present in the SPL (Figure 2.1). First cut being carbonaceous in nature with variable amounts of graphite (30-100%) obtainable above the collector bars. And below the collector bar, the second cut is obtained primarily for insulation, which mainly comprises of refractory materials. The composition of Spent Pot Lining (SPL) depends on several factors such as composition of new cell lining, operating conditions, etc. which is different for each technique. The dismantling procedure greatly affects the quantity of bath and frozen aluminium in the lining components[16].

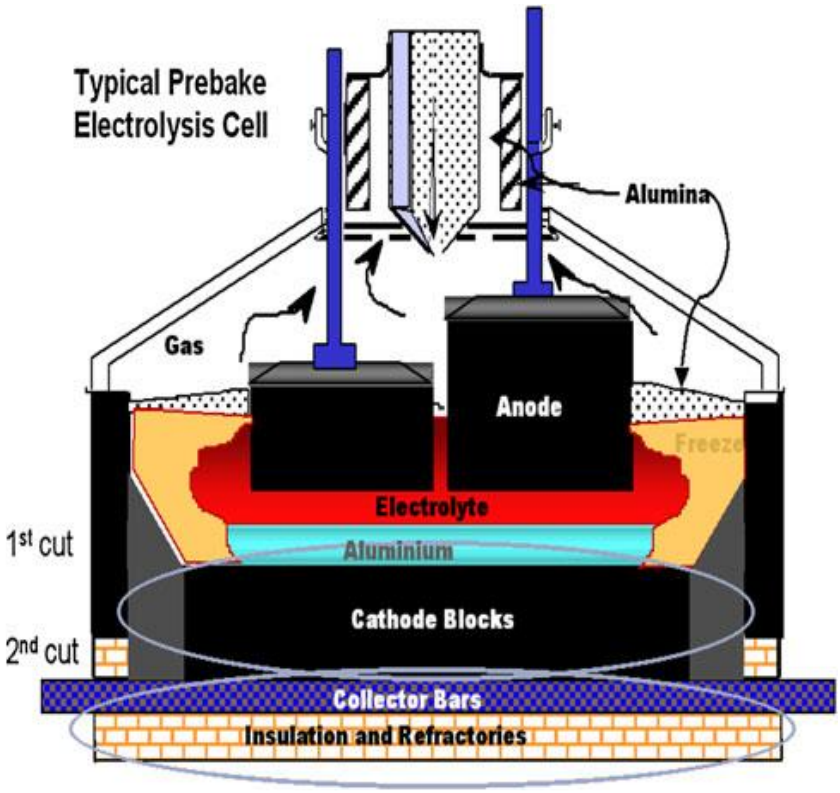


Figure 2.1: Schematic diagram of Hall-Heroultcell[16]

The operating period of the cell is a vital factor which generates varying composition of SPL. Depositions of Sodium and Sodium Fluoride inside the lining materials increase with longer cell operation. Composition of the SPL as obtained for three different technologies is given in Table 2.1 (type A and type B are different SS modern prebakes). The composition was obtained from a composite sample of both first and second cut of SPL reduced to 300 mesh. The yield of fluoride and cyanide concentration varies with adopted process. With changing conditions inside the cell, various side reactions tend to take place with time. So, a robust treatment process is needed to obtain safe by-product from SPL. Finally, the 1st and 2nd cut SPL would be separated during dismantling of pot. The concentration of fluorides and cyanides is found to be prominent in first cut SPL.

2.1.1 Spent Pot Lining (SPL) reactivity and toxicity

Generation of water-reactive chemicals (which may be inflammable and explosive) happens due to the subjection of SPL at high temperature during the electrolysis process. Varieties of fluoride, sodium and aluminium compounds, metal (Al, Li, Ca and Na), reactive metal oxides (Na_2O, Al_2O_3), nitrides and carbides are found in SPL. These compounds react with moisture and air to produce NaOH, H_2, C_2H_4 and NH_3.

Table 2.1: Composition of SPL for different technologies[16]

Elements	A type	B type	Soderberg	Major phases
Fluorides (wt. %)	10.9	15.5	18	Na_3AlF_6, NaF, CaF_2
Cyanides (ppm)	680	4480	1040	NaCN, $NaFe(CN)_6$, Na_3FeCN_6
Aluminium total (wt. %)	13.6	11	12.5	Al_2O_3, $NaAl_{11}O_{17}$
Carbon (wt. %)	50.2	45.5	38.4	Graphite
Sodium (wt. %)	12.5	16.3	14.3	Na_3AlF_6, NaF
Al metal (wt. %)	1	1	1.9	Metal
Calcium (wt. %)	1.3	2.4	2.4	CaF_2
Iron (wt. %)	2.9	3.1	4.3	Fe_2O_3
Lithium (wt. %)	0.03	0.03	0.6	Li_3AlF_6, LiF
Titanium (wt. %)	0.23	0.24	0.15	TiB_2
Magnesium (wt. %)	0.23	0.09	0.2	MgF_2

A procedure called wet delining was used earlier for the interruption of lining materials, which leads to formation of flammable gases. However, due to health, safety and environmental (HSE)[15] concerns, this practice is now abandoned and currently a dry process is used for lining removal. The toxic, corrosive and reactive nature of the material means that care must be taken in its handling, transportation (transportation containers must be ventilated) and storage (due to its leaching ability of fluorides and cyanides).

2.1.2 Handling possibilities for Spent Pot Lining (SPL)

There is a continuous effort by the aluminium industries to develop an economic method to recycle the heterogeneous SPL materials. Considering complete, partial and no recycling of SPL, the treatment approaches differ. For complete or partial recycling of SPL, pyrometallurgy or hydrometallurgy approaches can be considered. Researchers have proposed various processes and some of the important followed processes are given in Table 2.2 and 2.3. Due to heterogeneous composition of SPL the total recycling of SPL is a tremendous challenge. Primarily SPL is focussed on implementing as fuel because of its high percentage of carbon. In cement industry, a limited quantity of SPL is added in a cement kiln to improve the quality

of cement. The other industries using SPL are the mineral wool and the iron and steel industries. All hydrometallurgical approaches aiming for total recycling of SPL require a separation of the main components such as carbon, refractory materials and fluorides. Partial recycling and disposal is less severe and based on the economics, some specific mechanisms can be affected for recycling. For example, while the industry operates smelters with wet effluent treatment centres, cryolite recovery could be achieved for future use. Harmless disposal of SPL requires some kind of treatment to stabilize the leachable fluoride and to decompose all water-reactive compounds cyanides. The best way for every plant in operation to use the method that suits its mandate and legal boundaries.

2.1.3 Environmental legislation concerns

Previously, SPL was categorized as an industrial or mining waste and was disposed of in secure as well as insecure landfill sites, which currently require remediation. Currently it being treated as a hazardous waste termed as KO88 since 1988 in the United States[17]and tagged as a special waste in Canada. The new classifications required SPL to have special storage buildings with proper hazard maintenance protocol. For industries processing hazardous wastes, environmental regulations have become stricter and it became more difficult for the cement and steel industries to accept unprocessed SPL. Partial or total detoxification is a necessity before reusing the SPL.

2.1.4 Recent storage of SPL

The prescribed norms of various agencies and legislations decide the storage and processing of SPL. It is estimated that at least 50 % of the total amount of SPL is still stored away in buildings, waiting for treatment.

In countries like Norway and Iceland, SPL has been stored on the seashore, considering as a passive treatment, for allowing of sea leaching of soluble component. The leachable fluorides that are present in SPL, react with the calcium ions in seawater to form a stable calcium fluoride. From an extensive investigation by the University of Iceland[18] we got to know that the dumping pits did not have detrimental effects on shore communities.

2.1.5 Industrial practices of Spent Pot Lining (SPL)

The usage of SPL in various industries has been investigated over the years and some of the possible uses are highlighted in Table 2.2.

Table 2.2: Use of SPL in various industries

Industry	Approach and reason	Disadvantage or problems associated
Cement[19–24]	First cut SPL is used in the kiln of reasonable calorific value and presence of fluorides shrinks the kiln temperature.	(i)Need for transportation in a closed container. (ii)Maximum allowable limit for sodium and fluoride limits
Steel[25–27]	Additive to steelmaking because fluoride improves slag formation and small quantities of SPL can substitute for CaF_2	(i)Need for Transportation in a closed container. (ii)Limitation of use due to hazardous waste
Rockwool	First cut SPL used as an substitute for coke	Limited requirement of SPL
Alumina Plant	Co-processing SPL with salt slags by BEFESA process	

2.2. TREATMENT AND RECOVERY PROCESSES

Over the years many processes have been developed, out of which hydrometallurgical or pyrometallurgical processes were found to be suitable.

2.2.1 Industrial scale improvements

Varieties of furnaces have been tried, which include rotary kilns, roasters and specialized arc furnaces at various temperatures. Some of the industrial scale treatment process is shown in Table 2.3.

Table 2.3: Industrial scale treatment process for SPL

Treatment approach	Process condition and purpose	Advantages	Disadvantages
PYROMETALLURGY APPROACH			
ALCOA (Reynold) Gum Spring process[28]	Killing of cyanides in a rotary kiln and formation of industrial excess for road aggregates. Use of Limestone to fix fluorides.	Generation of inert valuable materials.	High temperature treatment approach. High cost for the treatment.
RT (Comalco) COMTOR[16,19,29]	Killing of cyanides in a pretreatment reactor. Residue leached with lime to yield liquor and kiln-grade Spar for cement industry.	Competition from other industry	High energy demand.
VORTEC process[15,16,19]	Generation of recyclable Industrial inert waste by combustion and pyrohydrolysis process.	Compromise in quality of product	High energy demand
AUSMELT process [16,19,22,30]	Creation of AlF_3 and reusable industrial waste.	Compromise in quality of product	High energy demand
Regain Process[16,31]	Fractional detoxification of SPL	Low temperature process for the destruction of simple cyanides to deactivate SPL	Still hazardous material
NOVA Pb[16]	Handling in rotary kiln at 1000°C	Calcicoke (High Carbon)\ Potentially recyclable products formation of useful product i.e. Calcifrit (High Fluoride and	High treatment cost
ELKEM process[6,16,22,32]	As a feedstock for pig iron making	Compromise in quality of product	Transportation problems and less requirement of feed
SPLIT process[16,19,30]	Treatment of SPL with $CaSO_4$ at 1000°C	Production of inert materials	High treatment cost
Plasma vitrification[16,30]	Inertization of SPL at high temperature	Generation of inert materials	High temperature treatment
HYDROMETALLURY APPROACH			
BEFESA [16,33]	Co-processing of SPL with salt slags	Creation of suitable machineries to be used in cement or mineral wool industry Low temperature requirement	Not Available
RIO TINTO ALCAN[16,22,31,34,35]	Low caustic leaching	Formation of Bayer liquor , CaF_2 and industrial waste can be used in other industry Low temperature requirement	High installation cost

2.2.2 Lab scale improvements

Various scientists have studied to ease the harmful effect of SPL by using different approaches and some of the developments are shown in the Table 2.4 and 2.5.

Table 2.4: Lab scale pyrometallurgical approach for SPL

Sl. No	PYROMETALLURGY APPROACH		
	Year	**Authors**	**Approach and Findings**
1	1997	V. A. Utkov et al.[36,37]	Water soluble NaCN neutralized by treating carbon rich part with $FeSO_4^-$
2	2000	Wang Y.[38]	Use as collar paste for protecting anode stems.
3	2000	Oliveira et al[22,39]	Heating up to more than 750°C to remove molten and volatile impurities
4	2000	Balasubramanian et al.[22,40]	Vitrification by adding small additions of glass former along with traces of nucleation agents to aid crystallization followed by melting at around 1300°C.
5	2001	Courbariauxet al. [22,29,41]	Treatment of crushed SPL in a circulating fluid bed
6	2004	Karpel S.[22,30] Li and Chen [16,22,42]	Heating of mix to about 1000°C, adding lime to oxidize cyanides and bind the fluoride
7	2007	Lazarinos[22]	Destruction of cyanide compounds in a gasification combustion
8	2007	Chen and Li [16,22,42]	Graphite and sodium in SPL make it sticky, slippery and difficult to crush. Chemical stability of the fluorides.

Table 2.5: Lab scale hydrometallurgical approach for SPL

Sl. No.	HYDROMETALLURY APPROACH		
	Year	**Authors**	**Findings**
1	1999	Baranovskii[22]	Mixing of crushed first cut SPL with that of limestone and then adding this mixture to an aqueous slurry for recovery of Soda and Potash
2	2001	Lu et al.[22]	Separation of aluminium electrolysis carbon froth and spent pot lining by froth flotation technique
3	2001	Zhao [43]	(i) SPL treated with water and H_2SO_4 to recover HF (ii) Filtration of the liquids for the manufacture of graphite powder, aluminium hydrate and alumina. (iii) Fluoride and sulfates are manufactured from filtrates
4	2001, 2002	Silveira et al.[24,44]	(i) pH of SPL was around 10-11.8 (ii) Total fluoride content was 5.13-11.41% (iii) Total dissolved fluoride at pH 12 and at pH 5 was 6.45-9.39% and 0.26-3.46% respectively
5	2002	Mirsaidov et al.[22]	Use of pine oil and kerosene as a flotation agent to separate cryolite alumina concentrate followed by burning of residual carbon at 800°C in rotary Furnace.
6	2007	Lisbona and Steel[45]	Leachability of NaF, CaF_2 and cryolite from SPL Precipitated fluorides in a form that can be recycled back into the pot have been studied by manipulating solution equilibria.
7	2008	Lisbona and Steel[30]	(i)Fluoride extraction of 76-86 mol. % (ii)Removal of NaF and Na_2CO_3 from SPL by water washing (iii)In pH 4.5-5.5 selective precipitation of fluoride as an aluminiumhydroxyfluoride hydrate product achieved by neutralization (iv)Higher pH leads to co-precipitation of hydrolyzed sodium fluoroaluminates
8	2012	Lisbona et al.[46,47]	(i)Leaching with Al^{3+} salts to precipitate aluminium hydroxyl fluoride hydrate (ii)Development of low-carbon environmentally sustainable approach
9	2012	Zhong-ning et al.[42]	(i)Two step alkaline-acidic leaching to achieve 65% leaching rate after NaOH treatment having 72.7% purity of carbon Leaching rate was increased up to 96.2% and purity of carbon up to 96.4%. (ii)Cryolite precipitation rate was 95.6% and purity of Na_3AlF_6 obtained is 96.4%.
10	2013	Lisbona et. al[48]	(i)Leaching behavior of SPL with aluminium nitrate and nitric acid (ii)Following an initial water wash at 60°C extracted a total of 96.3% of the remaining fluoride, extraction of Mg and Ca in form of MgF_2 and CaF_2.

2.3. CONCLUDING STATEMENT

The involvement of local communities and lawmakers has made the dumping of SPL in lined site a common practice by aluminium industry, ever since it has been considered as hazardous waste. However, due to the indefinite behaviour of its chemistry, there is no widely accepted technology available yet for large scale treatment of SPL. In recent years hydrometallurgical studies for the treatment of SPL have gained momentum because it is more energy efficient and has a better recovery rate for several valuable compounds. The presence of the free sodium layer makes the surface of the SPL slippery and difficult to crush which is another major challenge to find an alternative to the problem of crushing of SPL. Choice of proper reagents for the leaching and enriching of carbon is yet to be optimized for the treatment and recovery useful fluoride and graphitic carbon from SPL.

The review of literatures in this chapter confirms that most of the treatment processes are optimized by a conventional way putting in light the treatment by using any of the specific optimization techniques. The novel approach of treatment with various other acids needs to be planned as well as an evaluation of the differences between them is the one of the main objectives of this project. The treatment of SPL is considered to be one of the major challenges due to presence of highly leachable fluoride and cyanide content. Some of the specific objectives are as follows:

- Characterization of SPL material (SEM-EDX, FESEM-EDX, XRD, CHNS).
- Treatment of SPL with HCl for leaching of soluble fluorides and cyanides
- Treatment of SPL with NaOH, for leaching of soluble fluorides and cyanides
- Enrichment of the carbon percentage of SPL samples using leaching process.
- Optimizing the process parameters using Taguchi design.

The prime aim of this project is to find a way to enrich the carbon in SPL as a fuel, at the same time without causing any environmental hazards.

3. MATERIALS AND METHODS:

In this section, the details of process conditions, experimentations as well as purpose of this study have been discussed. All the experiments accompanying leaching were done in batch mode.

3.1. MATERIALS

3.1.1 Chemicals

All the chemicals were procured from Merck (Germany) and were established of an analytical reagent grade of the highest purity.

Table 3.1: Details of chemicals used

Type	**Name**	**Use**
Alkali	NaOH (pellets)	Preparation of Alkali leaching agent
Acid	HCl (35% Assay)	Preparation of acid leaching agent
Solvent	Deionized water	Preparation of stock solutions of alkali and acid.
Cleansing agent	Methanol	Cleansing of glassware

3.1.2 Glassware and instruments

All the glasswares that were used for experimentation, consisting of conical flasks, beakers, measuring cylinders, pipette, petri-dish, etc. were manufactured by Borosil.

3.2. METHODOLOGY

3.2.1 Sample preparation

For the planned study, we used first cut Spent Pot Lining (SPL) sample which was collected from Vedanta aluminium Ltd., Jharsuguda, Odisha, India. Once obtained, the SPL was dried at 110 ±1°C for 4 hrs, crushed in a ball mill and then sieved to recover preferred size fractions that can pass through the 52 BSS sieve (300 micron). The experimental process and setup is shown as photographs taken during the process, (Figure 3.1 (i) – (vii))

3.2.2 Water washing of Spent Pot Lining (SPL)

Initially, 100g of raw SPL was treated with 500ml of deionized water at 50 ±1°C for a period of 4 hours in an orbital shaker with rotation speed at 120rpm. The purpose of taking 5:1

L/S ratio was to leach out leachable fluorides at which optimal leaching was achieved. Complete water washing of SPL was done to neutralise the pH and bring it down to 6.8-7[44]. The soluble components were then filtered out by using a Macheray-Nagel MN 640 filter paper and the residual SPL was then dried in an oven for a period of 4 hours at 110 ±1°C. The formula for calculating leaching percentage is as follows:

$$\%Leached = [L_0 - L_e]/(L_0) \times 100$$

Where L_o is the initial weight of SPL before leaching process and L_e is the final weight of SPL after leaching process (in grams).

3.2.3 Leaching experiments

Once the water washed SPL was obtained, it was undergone through a series of leaching experiments. The first step was alkali leaching, followed by acid leaching. Each experimental step was conducted with a fixed amount of sample. Then the treatments were done at 120 rpm and 4 hours' time either in orbital shaker or magnetic stirrer depending upon the temperature requirement. After each experiment, the leachates were filtered out by MN 640 filter paper and the residue was dried in a hot-air oven for a period of 4 hours at 110 ±1°C, along with the filter paper. The weight of the filter paper was then subtracted to obtain the exact weight of the dried residue. After each treatment, the pH of the residue[44] was brought down to normal range as per standardized practice and then succeeding treatment or characterization was done.

The variables of the experiment were: acid concentration, alkali concentration, temperature, and L/S ratio. The choice of the values for each variable is discussed in the next paragraph.

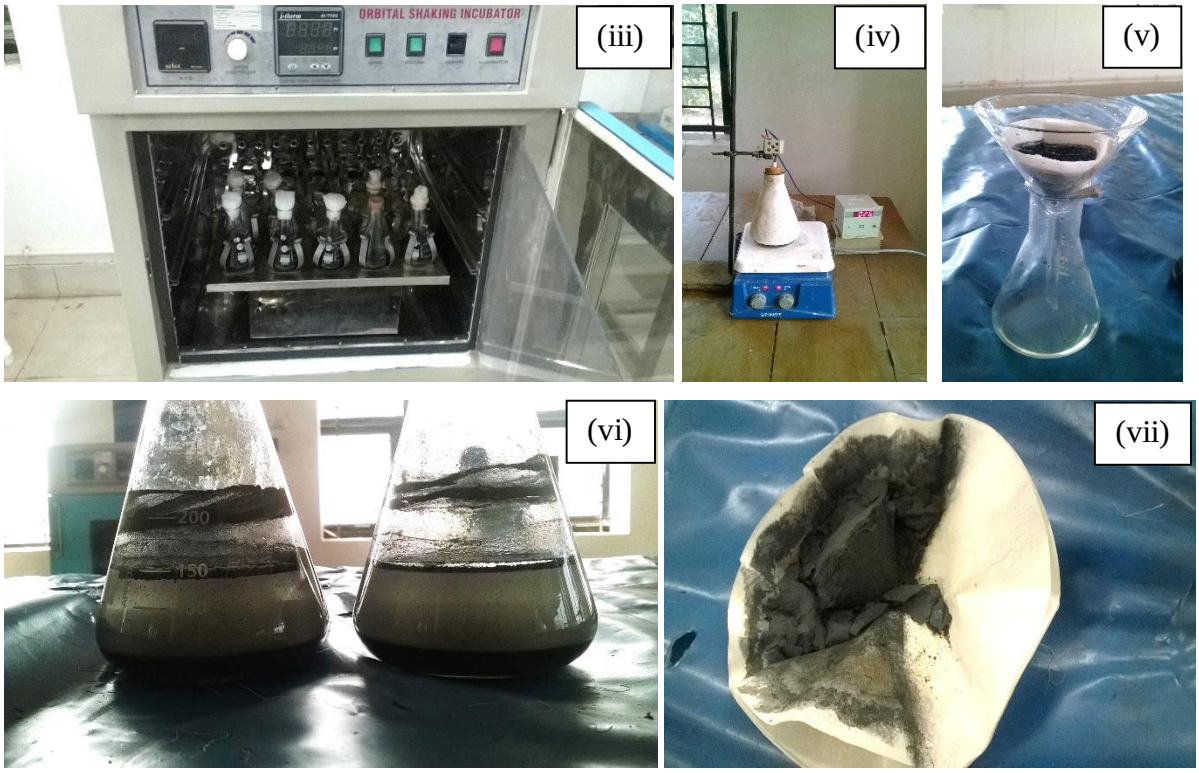


Figure. 3.1: Experimental setup: (i) Raw SPL blocks (ii) Powdered SPL (iii) Leaching at lower temperatures carried out in Orbital Incubator Shaker (iv) Leaching at higher temperatures carried out on hot plate with stirrer (v) Water washing and filtration of the samples (vi) Sample leaching after 4 hours (vii) Final oven-dried SPL sample

3.2.4 Design of experiment (DOE) and statistical analysis

Once the readings are recorded for each combination as specified by the Taguchi Design, various statistical analyses were carried out in order to find the optimum parameter in leaching. Regression plots, ANOVA were also carried out to further understand the nature of the data.

The Taguchi design method helps in finding the effect of the factors on distinctive properties and the optimum condition of the factors. This is considered to be one of the simplest and most efficient ways to optimize design for performance, cost and quality[49,50]. The advantage of the Taguchi optimization design over the conventional optimization techniques is that the experimental conditions are defined with least variability, whereas in conventional optimization it is determined on the base of measured values of the characteristic properties. In addition to the present Taguchi approach, analysis of variance (ANOVA) was also used as a tool of analysis, which can better approximate the effect of a factor on the characteristic properties and create orthogonal arrays for experiments. The signal/noise ratio was used to

measure the quality characteristics deviating from the preferred value in Taguchi method. The experimental conditions having the maximum signal to noise (S/N) ratio were taken as the optimal conditions, and the varying characteristics were found to be inversely proportional to the S/N ratio. The range of experiments is given in the Table 3.2.

Table 3.2: Ranges of experimental parameters for Taguchi design

Independent variables	**Levels**			
Acid concentration (M)	2.5	5	7.5	10
Alkali concentration (M)	0.5	1.5	2.5	3.5
L/S ratio (cm^3/g)	1.5	2.5	3.5	4.5
Temperature (°C)	25	50	75	100

Minitab: The design of experiments as well as optimization of the final responses was done using Minitab software. Minitab is a statistics package developed at the Pennsylvania State University by researchers Barbara F. Ryan, Thomas A. Ryan, Jr., and Brian L. Joiner in 1972. It is a highly useful tool in all kinds of statistical analysis across all domains.

Once the DOE (Design of Experiment) was done based on Taguchi model, the four independent variables and their parameters were entered in a Minitab worksheet. The software generated a specific table according to which the combination of experiments had to be done. A four factor, four level design was selected, which generated sixteen combinations of the four factors that contributed to the response (leaching percentage):

Table 3.3: Combination of factors in DOE by Taguchi Design.

Sl. No	Temperature	Alkali Conc.	Acid Conc.	L/S (cm3/g)
1	25	0.5	2.5	1.5
2	25	1.5	7.5	4.5
3	25	2.5	10	2.5
4	25	3.5	5	3.5
5	50	0.5	5	2.5
6	50	1.5	10	3.5
7	50	2.5	7.5	1.5
8	50	3.5	2.5	4.5
9	75	0.5	7.5	3.5
10	75	1.5	2.5	2.5
11	75	2.5	5	4.5
12	75	3.5	10	1.5
13	100	0.5	10	4.5
14	100	1.5	5	1.5
15	100	2.5	2.5	3.5
16	100	3.5	7.5	2.5

3.3. CHARACTERIZATION OF SPENT POT LINING (SPL) SAMPLES.

Characterizations of the SPL sample were done by several techniques to get the broader idea of all the components present in the SPL. Four characterization methods were followed to get best results in each case. The purpose and operating conditions of the experiments are emphasized in the Table 3.4. For XRD analysis, the phases of all the materials used were identified by the standard software provided with the XRD instrument i.e. “X’Pert Highscore” version 1.0b.

Table 3.4: Instruments used and purpose

Instrument	Make	Operation conditions Or specification	Purpose
Analytical balance	Sartorius (BS223S)	1mg - 100g	Weight measurement
Incubator shaker	Environmental orbital Shaker	• Speed: 120 rpm. • Temperature:25 and 50 ±1 °C.	Shaking of conical flasks used in leaching experiment
Scanning Electron Microscope-Energy-dispersive X-ray spectroscopy	JEOL (JSM-6480 LV) and Nova Nanosem 450 by BRUKER by FEI	• Magnification: up to 10000X • Resolution : 1μm • Detector: EverhardtThornley secondary electron detector and Solid state backscattered detector. • X-Ray Analysis: Oxford Instruments ISIS 310 system with "windowless" detector. • Light element analysis: silicon detector with ATW.	Morphological study about the structure and extent of leaching capacity of SPL, and the elemental analysis of samples.
CHNS analyzer	ElementarVario El Cube CHNSO.	• Measurement of carbon, hydrogen, nitrogen and Sulfur of the SPL sample • Initial wt.- under 10mg	Ultimate analysis-ASTM-D-3176 for Elemental Analysis
X-ray diffraction analysis	Philips X'Pert X-ray diffractometer	• Cu Kα radiation generated at 35 KV and 30 MA • Scattering angle 2θ was ranged from 5° to 80° • scanning rate of 3 degrees/minute	Mineralogical and phase analysis of SPL samples.
Hot Air Oven	WEIBER	• Done at 110 ±1°C for 4 h maximum	For drying of samples
Magnetic Stirrer	Spinot-Tarson, Spectro	• Speed: 120 rpm • Temperature:75 and100±1°C.	For Stirring at high temperatures
Oven and furnace	Weiber, Adco-electric furnace	• As per standards	For proximate analysis[30] ASTM-D-3172,3173,3174,3175

4. RESULTS AND DISCUSSION:

4.1. TAGUCHI APPROACH FOR OPTIMIZATION

The main objective of the optimization techniques was to find out the optimum parameters for leaching, as well as to know the effect of acid concentration, alkali concentration, temperature, L/S on the leaching percentage in terms of percentage contribution. The word "signal" signifies the desirable value (mean) for the output characteristics and the word "noise" indicates the undesirable value (SD) for the output characteristics in Taguchi method. The Taguchi method uses the S/N ratio to measure the quality characteristic deviating from the desired value. The "larger is better" option was selected for the optimum leaching percentage calculation. The Signal to Noise (S/N) ratio Y was determined by means of following equation,

$$Y = -10 \log \sum_{k}^{n} \binom{n}{k} x_k^{-2} \qquad (4.1)$$

Where n is the number of test and x_k are the comparison variables in the k^{th} experiment.

Table 4.1: The experimental values for leaching percentage under different conditions

Sl no.	Alkali Conc.	Acid Conc.	L/S (cm3/g)	Temperature	Leaching %	S/N Ratio
1	0.5	2.5	1.5	25	31.25	29.8970
2	1.5	7.5	4.5	25	41.44	30.6627
3	2.5	10	2.5	25	42.7	32.9143
4	3.5	5	3.5	25	50.95	34.1002
5	0.5	5	2.5	50	34.13	33.9236
6	1.5	10	3.5	50	48.87	33.8358
7	2.5	7.5	1.5	50	48.18	32.3484
8	3.5	2.5	4.5	50	52.86	33.7808
9	0.5	7.5	3.5	75	44.23	34.4296
10	1.5	2.5	2.5	75	49.68	34.6656
11	2.5	5	4.5	75	54.11	33.6573
12	3.5	10	1.5	75	47.7	32.6086
13	0.5	10	4.5	100	50.7	34.4625
14	1.5	5	1.5	100	49.14	34.1429
15	2.5	2.5	3.5	100	52.66	34.1599
16	3.5	7.5	2.5	100	51.05	33.5704

From the main effect plot for S/N ratio and from the equation, it was observed that greater the value of S/N ratio obtained, smaller was the variance of leaching percentage around the desired value. From Figure 4.1 it can be recognised that more the significance of the result of the parameter, the deviance from the horizontal line was more. However, the relative importance among the factors for leaching percentage calculation still needs to be known so that ideal combination of the process parameter levels can be calculated more accurately. It was explained through the analysis of variance of S/N ratio.

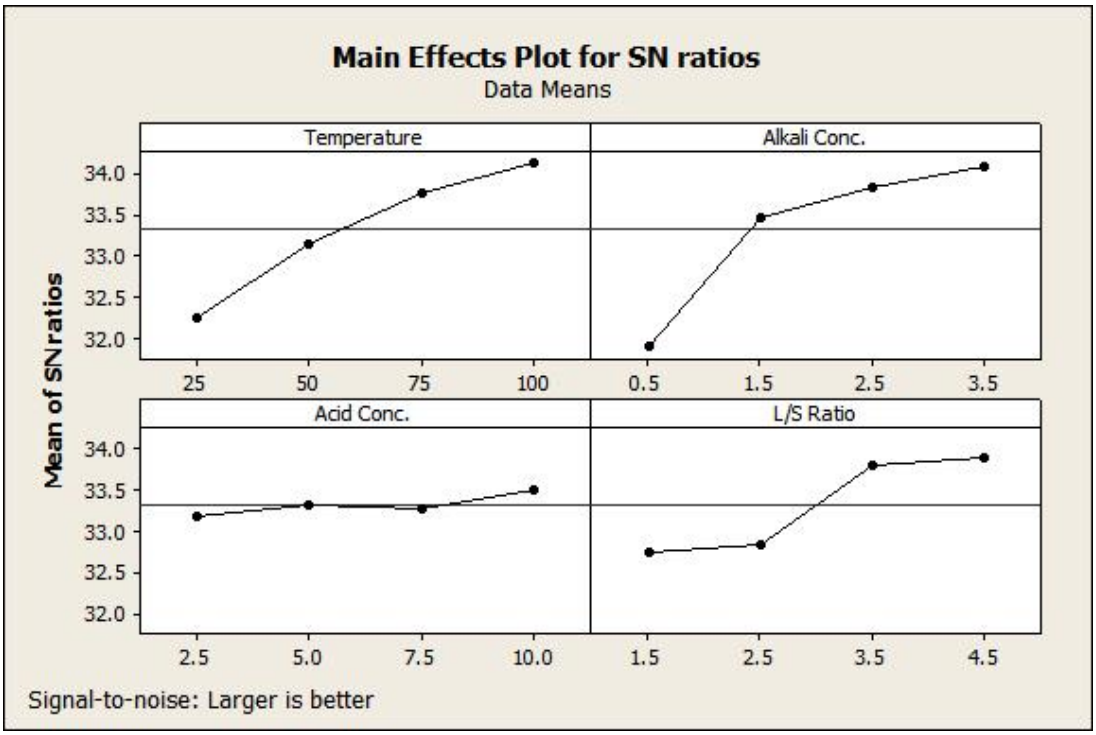


Figure 4.1: Main effect plot for SN Ratios of the Taguchi optimization

4.2. ANALYSIS OF VARIANCE (ANOVA)

ANOVA is a collection of statistical models used to analyse the differences between group means and their associated procedures. The reason for performing ANOVA was to investigate which parameters significantly affect the quality characteristics. A procedure called as “Fisher (F)” test was conducted to identify the significant effect on the quality characteristic. The “F” value is the ratio of the mean of the squared deviations to the mean of squared errors. Usually, a higher value of F indicates that the process parameter has a significant effect on the quality characteristics. The results of analysis of variance (ANOVA) for leaching percentage at various process conditions are presented in Table 4.2. After the selection of optimal level of

the process parameters, the final step was to calculate and validate the improvement of the quality characteristics using the optimal level of the process parameters. The probable S/N ratio using the optimal parameters for leaching percentage can be attained and the related other factors can be calculated by the Eq. (4.1). From Table 4.2 it was found that alkali concentration was the most significant factor whereas acid concentration was the least significant factor among all the independent factors or parameters (according to percentage contribution), in case of hydrochloric acid.

Table 4.2: Analysis of variance of Signal to Noise (S/N) ratio

Source	DF	Seq SS	Adj SS	Adj MS	F	P	% Contribution
Alkali concentration	3	11.6485	11.6485	3.88284	3.72	0.154	47.27
Acid concentration	3	0.2426	0.2426	0.08086	0.08	0.968	1.02
L/S ratio	3	4.5779	4.5779	1.52596	1.46	0.381	18.55
Temperature	3	8.1524	8.1524	2.71747	2.61	0.226	33.16
Residual Error	3	3.1289	3.1289	1.04297			
Total	**15**	**27.7503**			**7.87**		**100**

S = 0.221 R-Sq = 98.7% R-Sq (adj) = 93.6%

4.3. RESIDUAL PLOTS

The option of all the four residual plots are selected to present them in a single graph for comparing the plots to assess various tests in order to check whether the proposed model fits the assumptions of the analysis or not. The residual plots in the graph comprise of:

i. Normal probability plot specifying whether the data are normally distributed, further variables are inducing the response, or outliers exist in the data.
ii. Histogram signifying whether the data are skewed or if outliers exist in the data.
iii. Residuals versus fitted values specifying whether the variance is constant and linear, a nonlinear relationship subsists, or outliers exist in the data.
iv. Residuals versus order of the data indicating whether there are methodical effects in the data due to time or data collection order.

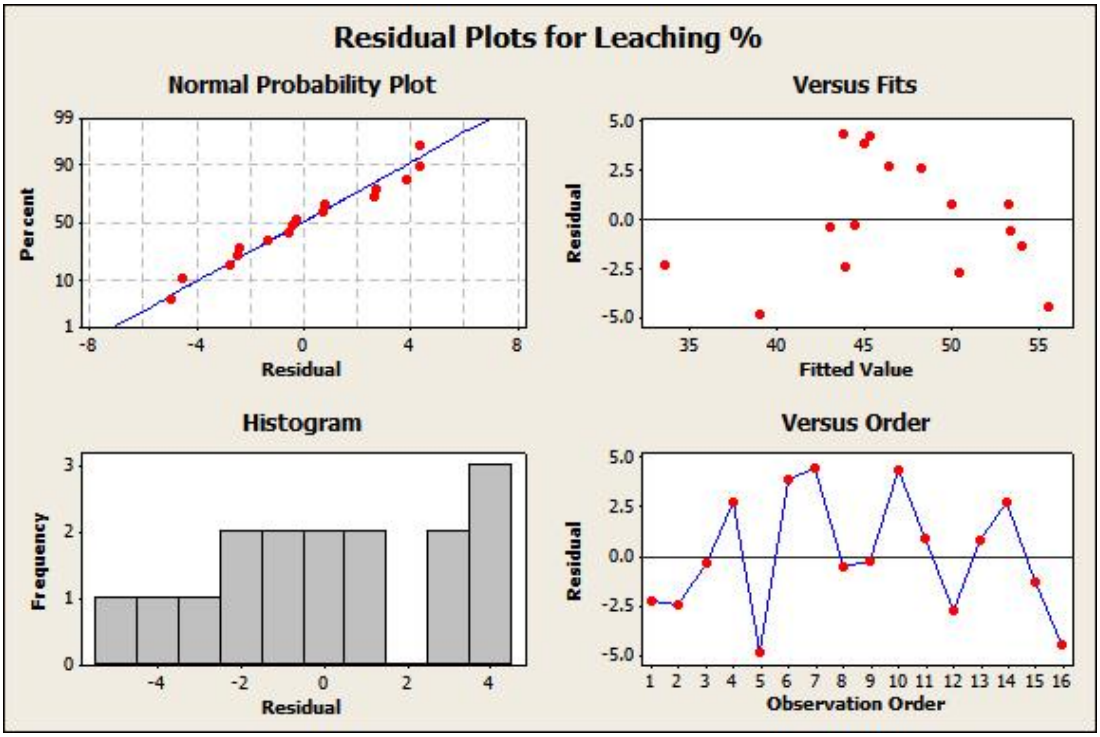


Figure 4.2: Four in one residual plot for leaching percentage of HCl treatment.

Figure 4.2 indicated that the residuals were almost falling on a straight line, which means that residuals were normally distributed and the normality assumption is practically valid. The suitability of ANOVA model was also tested through the comparison between calculated and experimental values, which is shown in scattered plot i.e. residual and fitted value. Additionally, the standardized residuals also displayed a random, irregular pattern, as detected in the residual versus observation order plot. This corroborates that the experimental data has been attained purely on random basis with no definite trend in the residual data. This also validates the impartiality of the data. The validity of the model assumptions for leaching percentage was therefore established from the residual plots.

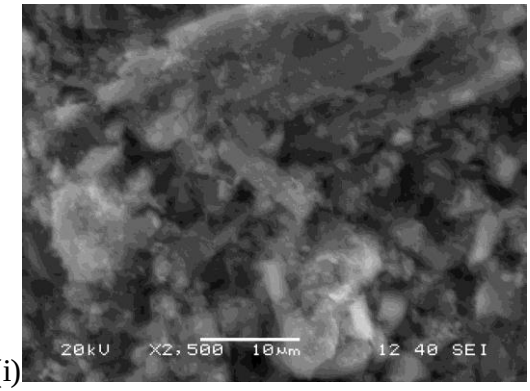
4.4 CHARACTERIZATION

Characterization of the different SPL samples (based on process parameters) were done using X-Ray Diffraction (XRD), Scanning Electron Microscope-Energy Dispersive X-ray Spectroscopy (SEM-EDX), Field Emission Scanning Electron Microscopy, and Carbon-Hydrogen-Nitrogen-Sulphur Analyser (CHNS).

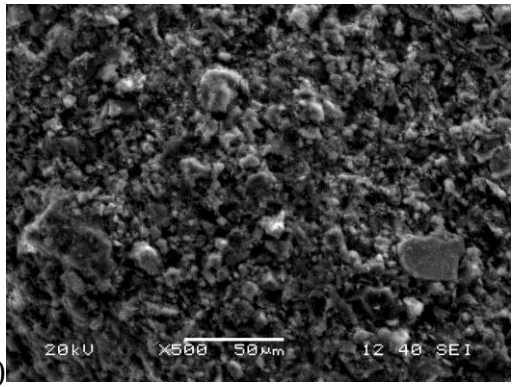
4.4.1. SEM-EDX and FESEM-EDX

The SPL particles under magnification seem to mainly comprise of carbonaceous graphitic particles and finely separated inorganic materials attached to the exposed surfaces. The occurrence was identified as due to cracking along the inside layers of bath material (cryolite and salts) between the layers of graphene[2,30,46–48]. In Figure 4.5 and 4.6, it was observed that a limited mineral exposure of the inorganic materials from the carbon fraction existed to a great extent, leading to better leachability. The inference was that most of the inorganic fractions remained attached to the darker graphite particles, and they covered the surfaces in a moderately thin layer of around 1 μm, and these inorganic segments were fully accessible to the basic and acidic leaching solutions. The observed darker regions were confirmed as the graphitic part, and the lighter regions were found to be the inorganic fractions, later confirmed from EDX analysis of a specific scan area. The presence of inorganic fractions was becoming less visible due to removal of leachable components which lead particles of lesser brightness being present in the materials (Figure 4.3, 4.4, 4.5 and 4.6). Finally, the ultimate analysis (CHNS) was done for the SPL samples and results are tabulated in Table 4.3.

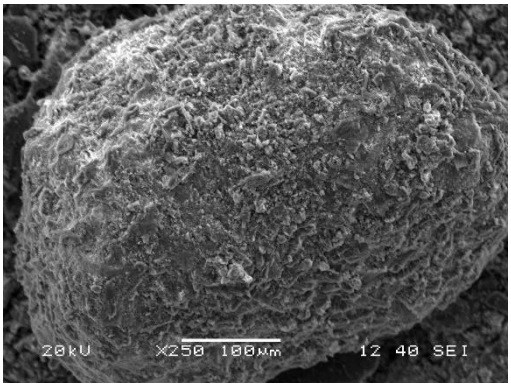
(i)



(ii)



(iii)



Element	Weight%	Atomic%
C K	33.27	43.96
O K	23.39	23.20
F K	22.68	18.94
Na K	17.07	11.78
Al K	3.59	2.11
Totals	100.00	

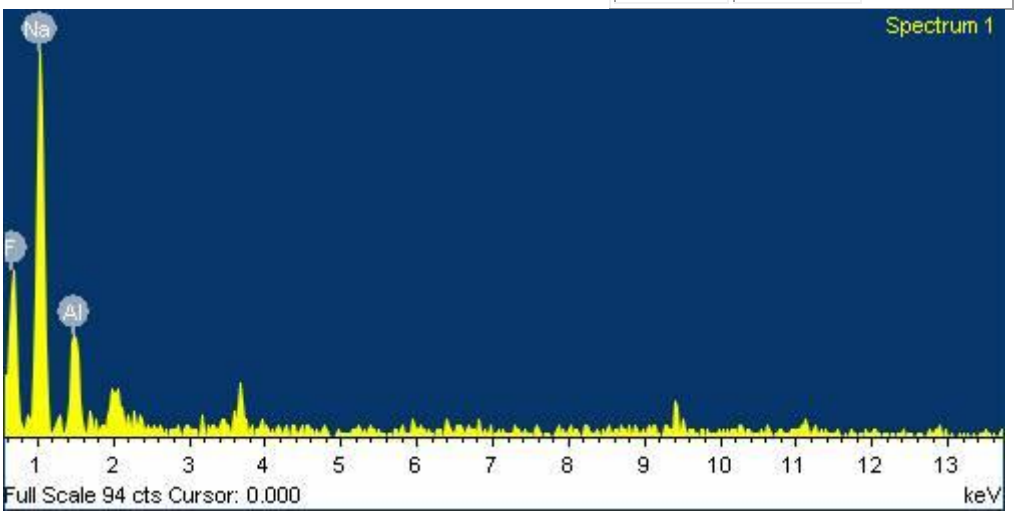
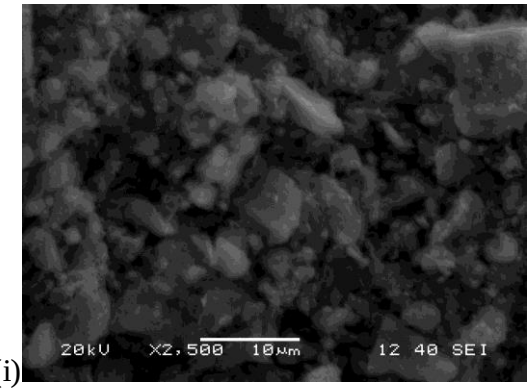
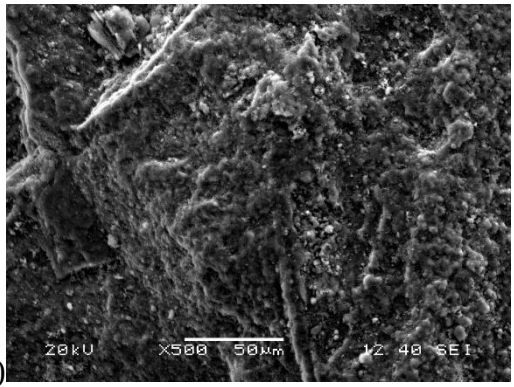


Figure 4.3: SEM-EDX images of raw SPL sample of magnifications 10 µm, 50 µm, and 100 µm. (i, ii & iii)

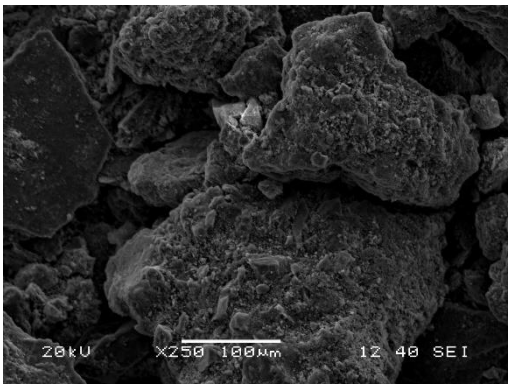
(i)



(ii)



(iii)



Element	Weight%	Atomic%
C K	43.94	58.84
F K	34.44	29.16
Na K	9.83	6.88
Al K	4.09	2.44
Ca K	4.21	1.69
Fe K	3.49	1.01
Totals	100.00	

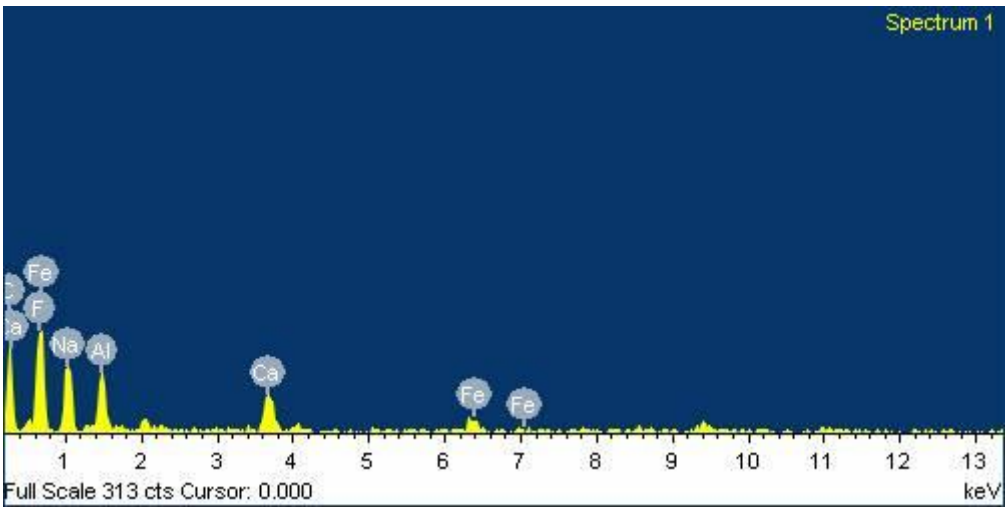
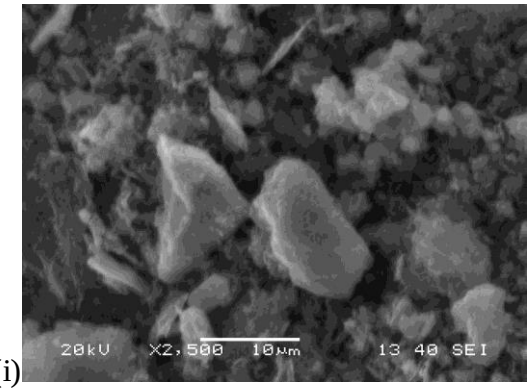
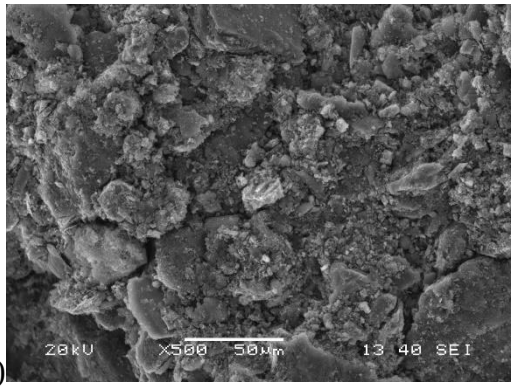


Figure 4.4: SEM-EDX images of water washed SPL sample of magnifications 10 µm, 50 µm, and 100 µm. (i, ii & iii)

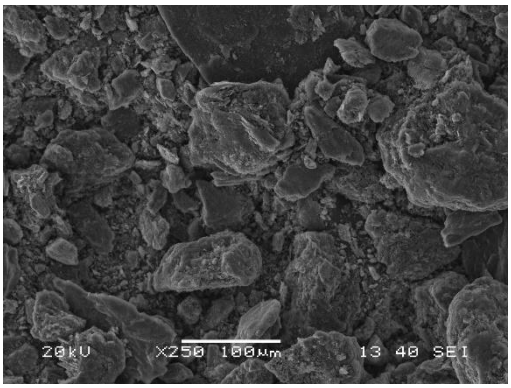
(i)



(ii)



(iii)



Element	Weight%	Atomic%
C K	74.20	81.12
O K	19.86	16.30
Al K	1.54	0.75
Si K	2.80	1.31
Ca K	1.60	0.53
Totals	100.00	

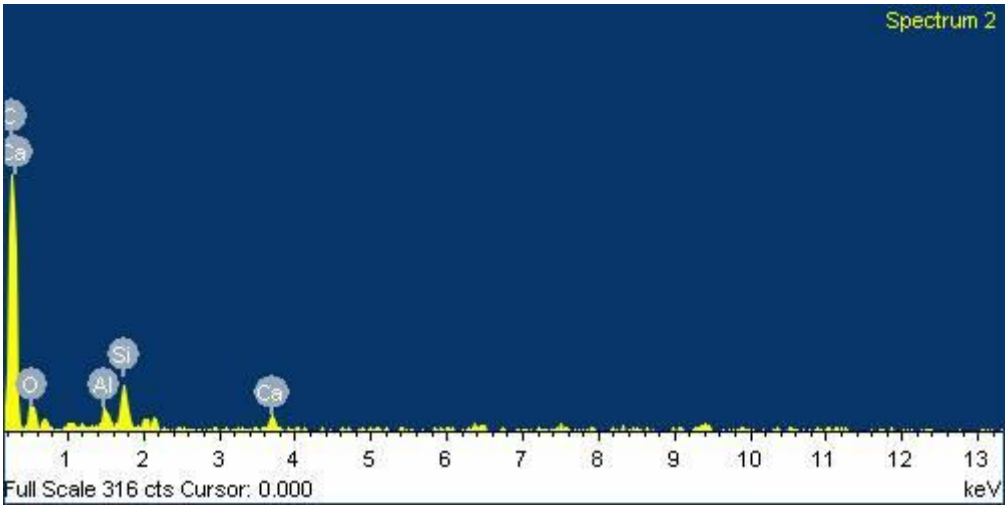
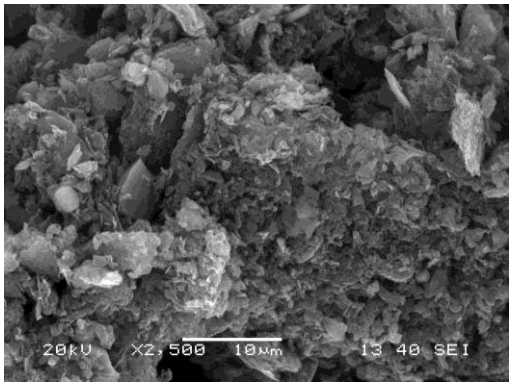
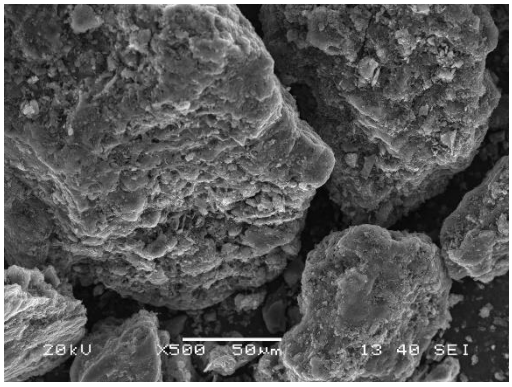


Figure 4.5: SEM-EDX images of alkali treated SPL sample of magnifications 10 µm, 50 µm, and 100 µm(at 1.5M NaOH concentration) (i, ii, iii)

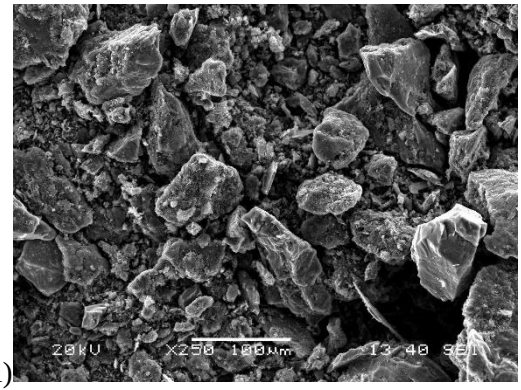
(i)



(ii)



(iii)



Element	Weight%	Atomic%
C K	86.78	90.42
O K	10.60	8.29
Na K	0.92	0.50
Al K	1.69	0.78
Totals	100.00	

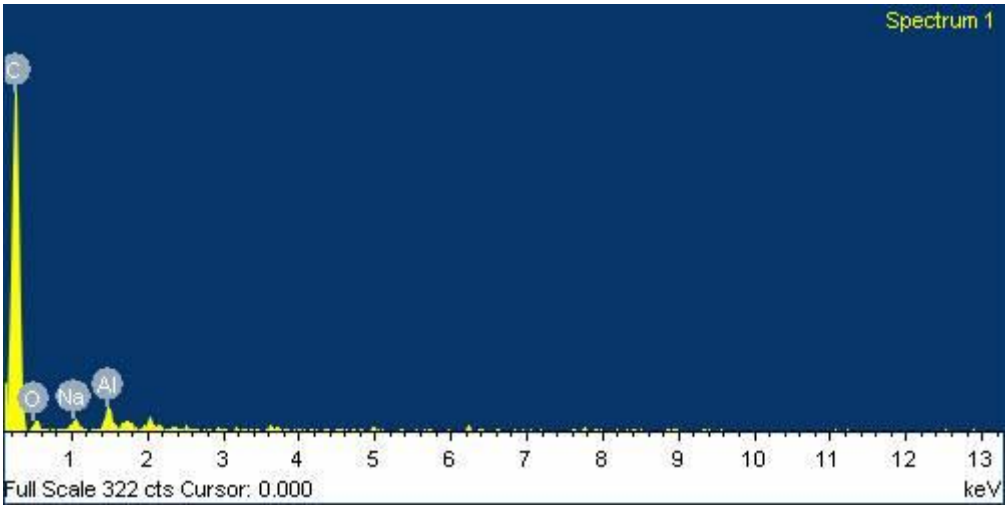


Figure 4.6: SEM-EDX images of the final HCl treated SPL sample of magnifications 10 µm, 50 µm, and 100 µm(i, ii & iii)

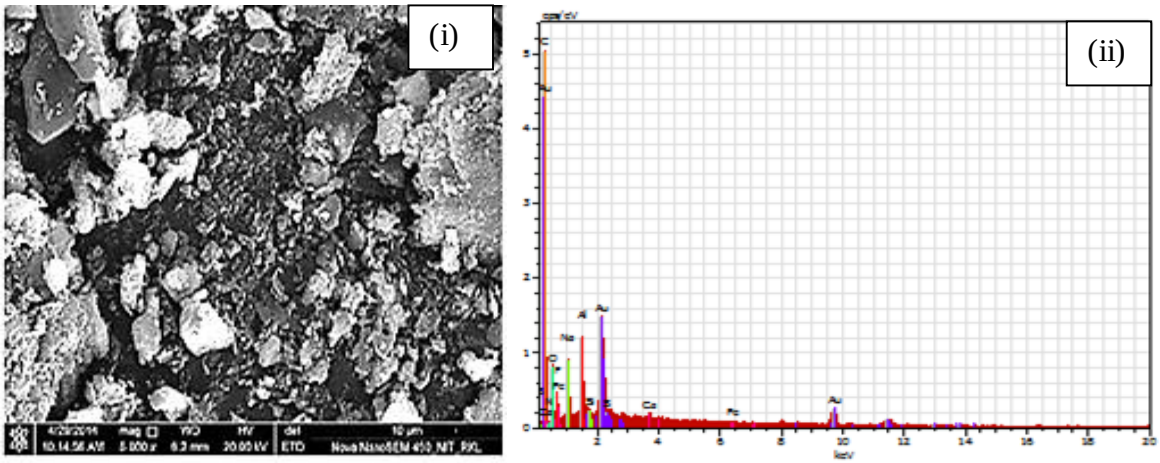


Figure 4.7: FESEM-EDX images of raw SPL (i, ii)

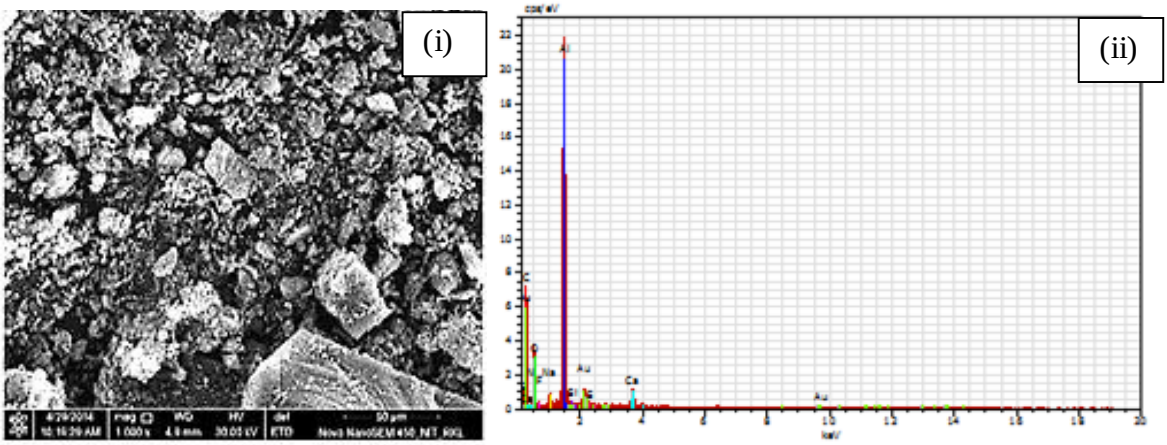


Figure 4.8: FESEM-EDX images of 1.5M NaOH treated SPL(i, ii)

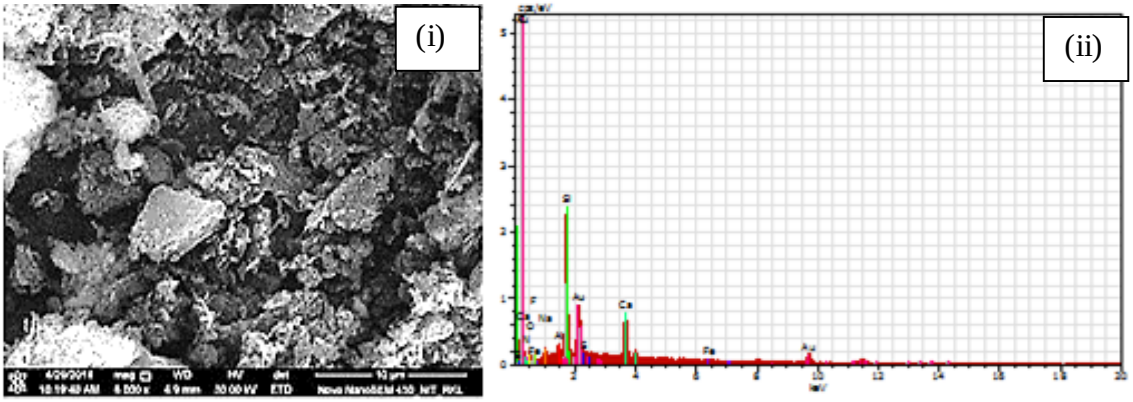


Figure 4.9: FESEM-EDX images of Final HCl treated SPL (i, ii)

4.4.2. Ultimate and Elemental analysis of SPL

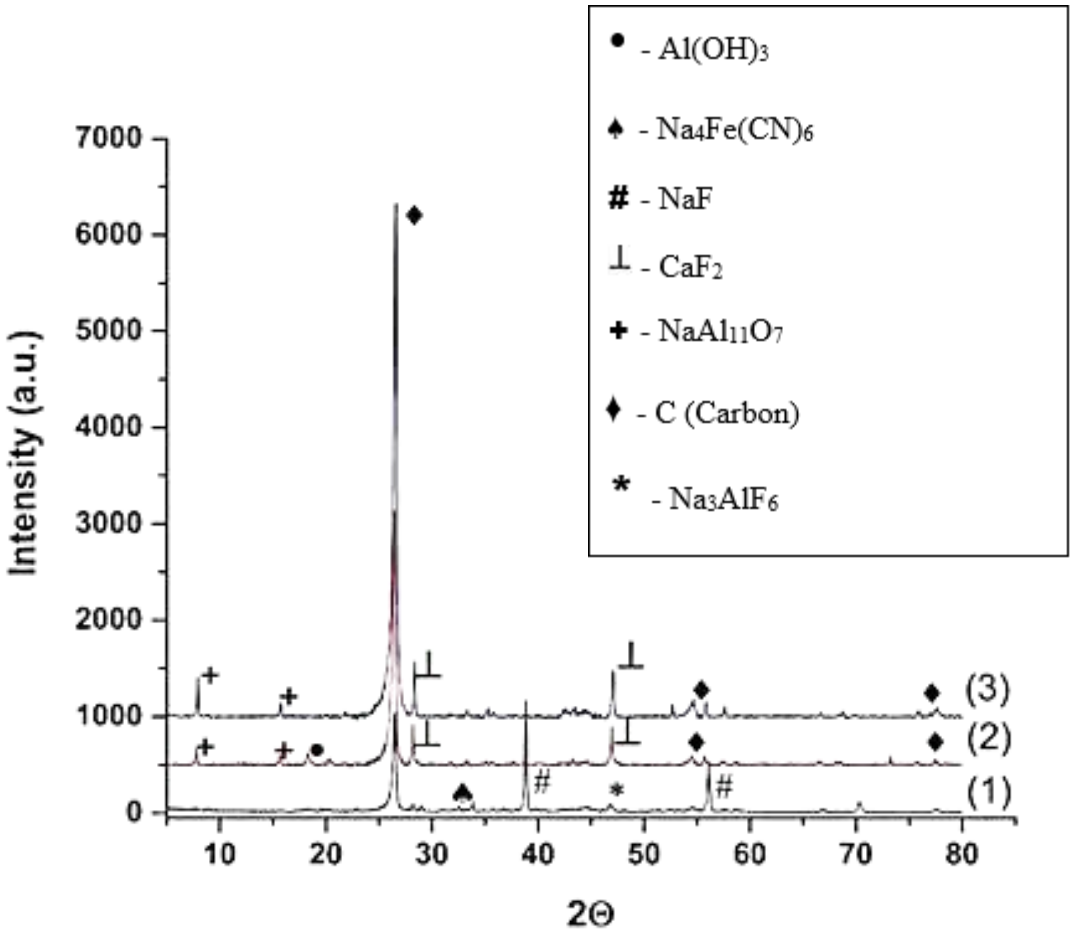
For the elemental compositions of the different SPL samples, CHNS analyser was primarily used. It was also used to establish the presence of the heteroatom constituent in each fraction which had changed after acid treatment of SPL. Another reason was to determine the hydrogen to carbon ratio for each fraction, which gives information about the aromaticity and the expected H_2 reduction during leaching of SPL. From the Table 4.8 it was established that the aromaticity has no noteworthy influence with increase in acid concentration, while the heteroatom compositions had been increased by acid treatment as the sulfur content had relatively increased, although no such incremental trend could be ensured. There was an increase of carbon content from raw SPL (43.39%) to HCl (70.44%) treatment, while the other parameters were kept constant (i.e. 4.5 L/S ratio, 10 M acid, and temperature 100 ºC).

Table 4.3: Ultimate and elemental analysis of SPL samples (CHNS)

Component	**Weight percentage (%)**						
	C	**H**	**N**	**S**	**H/C**	**N/C**	**S/C**
Raw SPL	43.39	0.626	0.59	1.27	0.0146	0.013984	0.029391
Water Washed SPL	48.18	0.25	0.42	1.71	0.00435	0.008318	0.035769
5 M HCl treated SPL	66.17	0.25	0.56	2.58	0.00405	0.008883	0.042096
10 M HCl treated SPL	73.44	0.21	0.53	3.43	0.00356	0.007486	0.048659

4.4.3 X-ray diffraction (XRD) analysis

The XRD analysis of optimum final treated sample, alkali treated sample, along with that of raw SPL was performed. The peaks of graphitic carbon (C), fluorite (CaF_2), villaumite (NaF), cryolite (Na_3AlF_6), sodium iron cyanide ($Na_4Fe(CN)_6$) and gibbsite ($Al(OH)_3$) phases were found. After washing and filtering of alkali treated SPL, insoluble ionic compounds like CaF_2, $Al(OH)_3$ and $NaAl_{11}O_{17}$ were found, and is shown in Figure 4.10.



LEGEND

- Raw SPL
- Alkali treated SPL
- Final acid treated SPL

Figure 4.10: XRD analysis of SPL samples

4.5. COMPARISON OF LEACHABILITY OF VARIOUS ACIDS

From F-test results, alkali concentration was found to contribute the most towards the outcome of an optimum leaching percentage. So a graphical comparison was made between the leaching percentages of HCl, HNO_3, H_2SO_4, $HClO_4$ [46] at four values of temperatures (25, 50, 75 and 100 ^oC) to find out the best suitable acid, since alkali concentration and temperature both contributed notably to the leaching percentage. The graphs are shown in Fig. 4.11, 4.12, 4.13, 4.14.

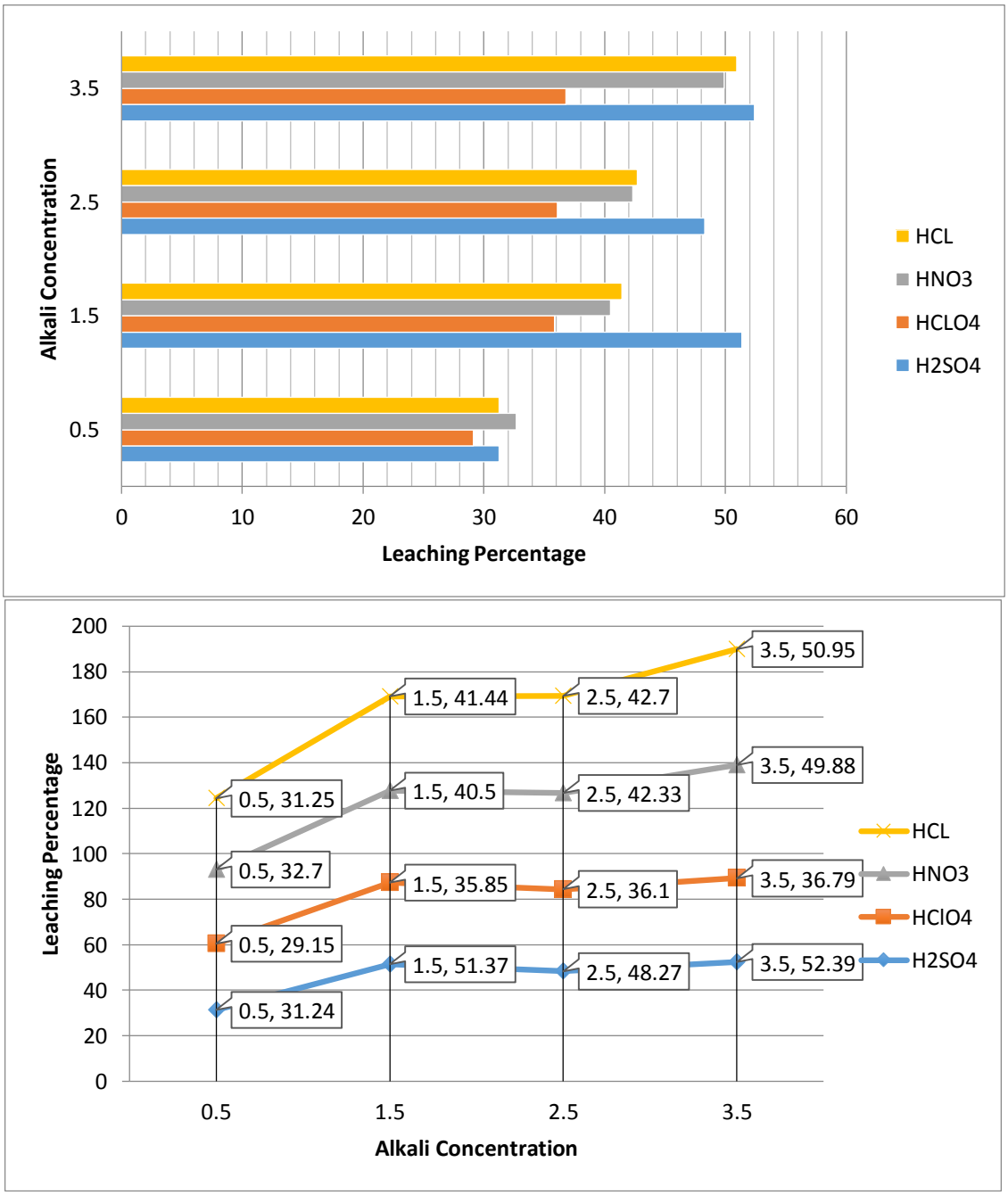


Figure 4.11: Graphical comparison of leaching percentage using HCl, HNO_3, $HClO_4$, H_2SO_4, at 25^oC a) Clustered Bar b) Stacked Line

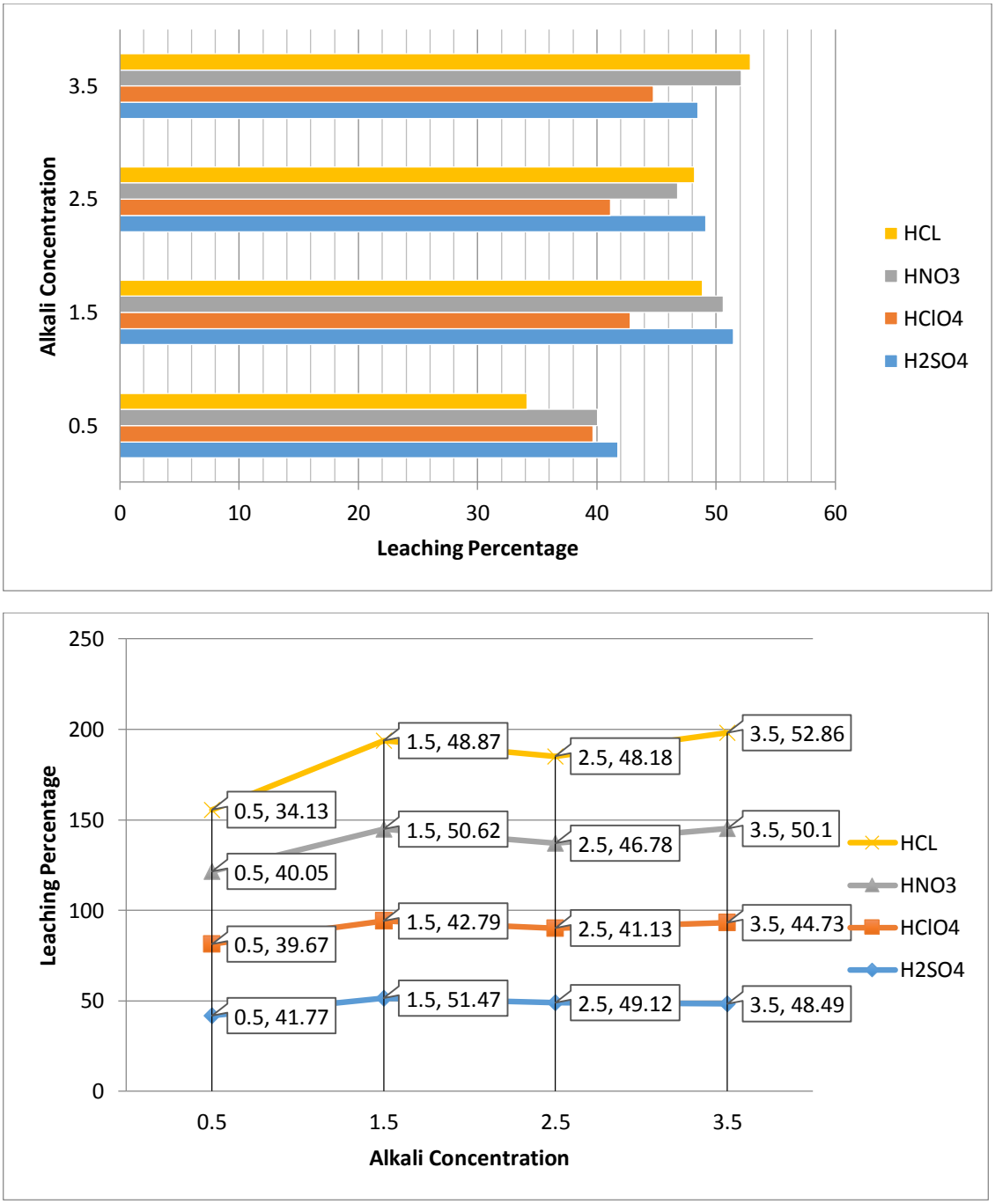
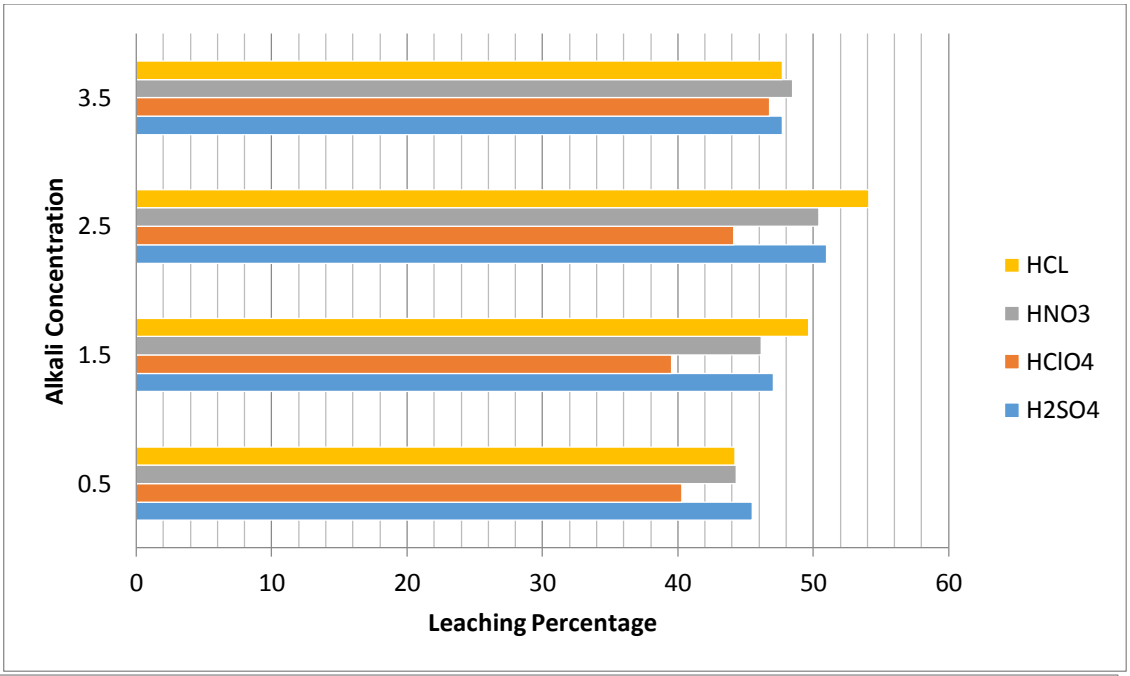


Figure 4.12: Graphical comparison of leaching percentage using HCl, HNO_3, $HClO_4$, H_2SO_4 at 50°C a) Clustered Bar b) Stacked Line



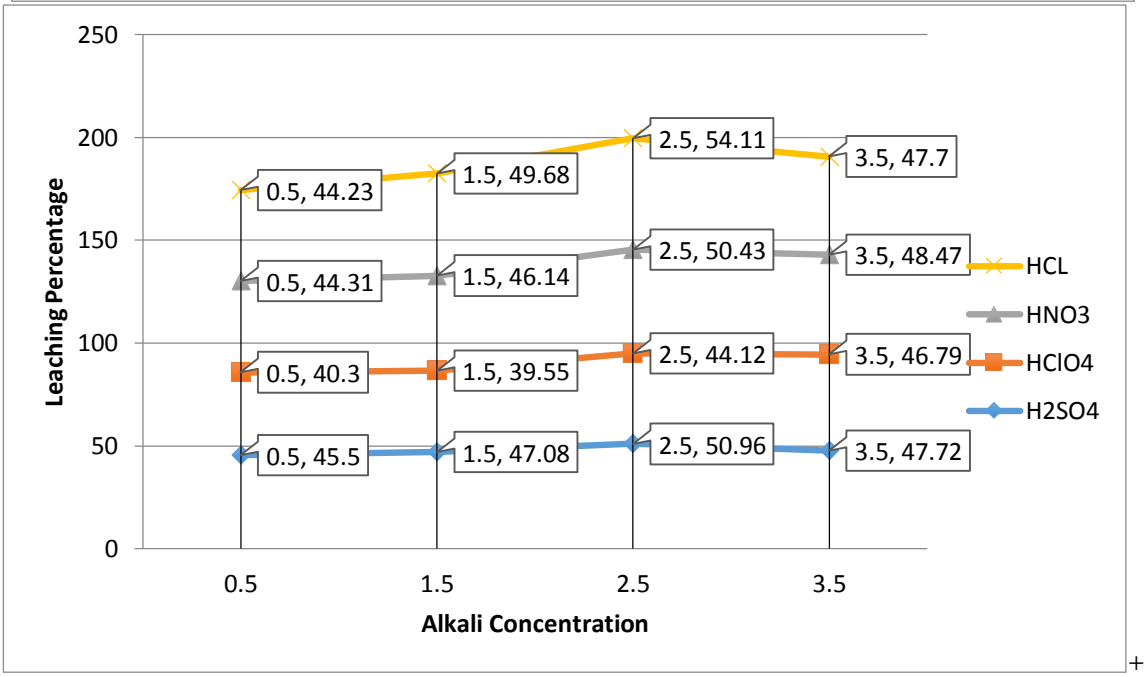


Figure 4.13: Graphical Comparison of leaching percentage using HCl, HNO_3, $HClO_4$, H_2SO_4, at 75°C a) Clustered Bar b) Stacked Line

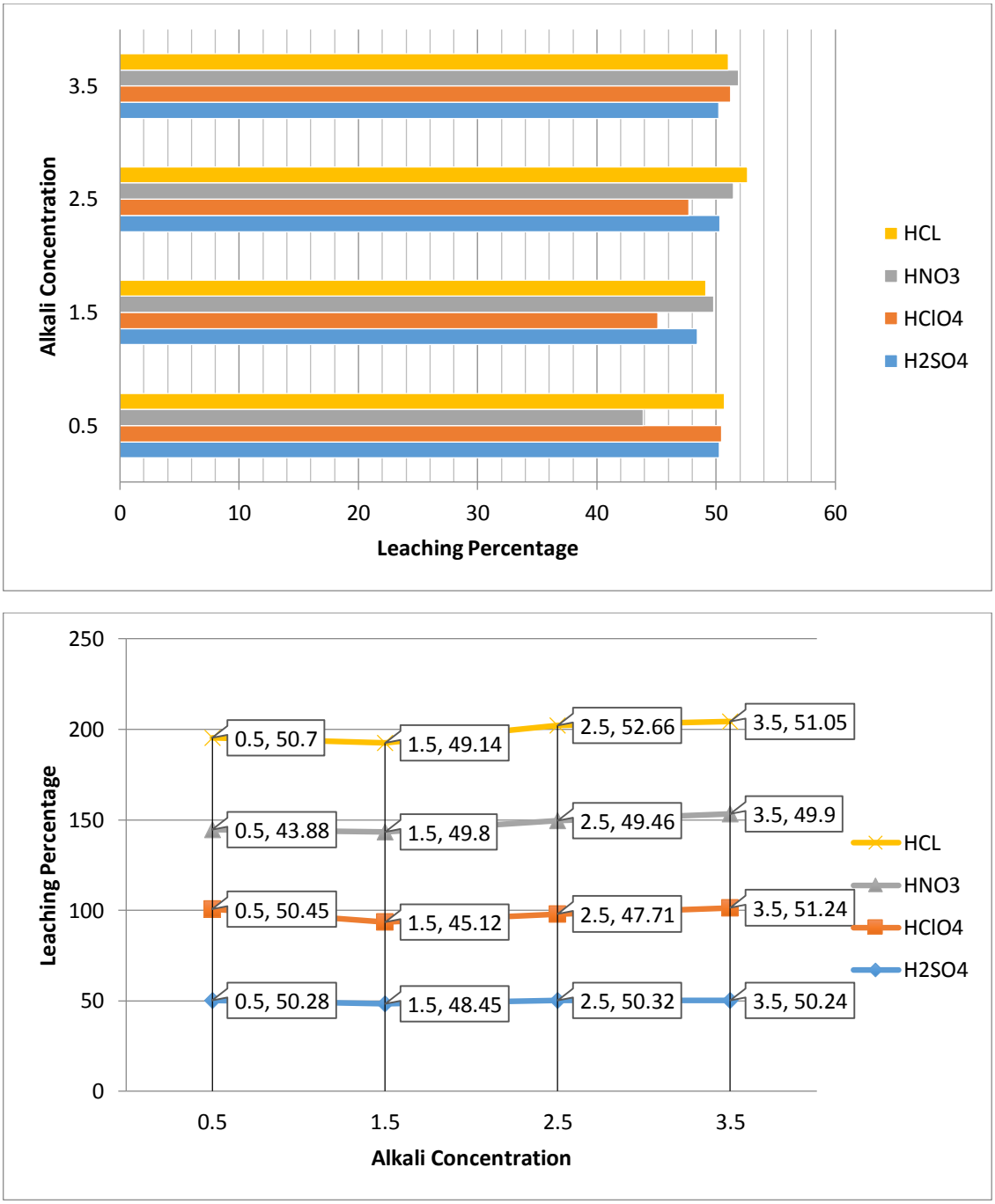


Figure 4.14: Graphical Comparison of leaching percentage using HCl, HNO_3, $HClO_4$, H_2SO_4, at 100°C a) Clustered Bar b) Stacked Line

4.6. OUTCOME OF THE STUDY

- The most significant factor was found to be alkali concentration, whereas the acid concentration was the least significant among the four parameters studied.
- Alkali concentration contributed 47.27% in the leaching process among the four factors, whereas acid concentration contributed only 1.02 %. The maximum leaching percentage was found to be 54.11% for Taguchi optimization method.
- S/N ratio analysis resulted in finding the optimum conditions at 2.5 M HCl, 1.5 M NaOH concentration, , 2.5 L/S ratio and at 75°C, which had a value of 49.68 %. Taguchi method suggested that 2.5 M HCl, 3.5 M NaOH, 3.5 L/S ratio and temperature of 100°C was found to be the ideal conditions for leaching.
- From the ultimate analysis (CHNS), the carbon percentage of SPL was increased from 43.39% to 70.44% and as confirmed from EDX data analysis, the carbon percentage was increased from 33.27% to 86.78%.
- At smaller temperatures, leaching percentages were also smaller (for lower values of alkali concentration). But as the temperature increased to 100°C, the leaching percentage value hovered at around 50% irrespective of the acid. At 100°C, all four acids (HCl, $HClO_4$, HNO_3, H_2SO_4) showed an equal amount of leaching percentage, for all values of alkali concentration.

4.6.1. Effect of fluoride solubility as a leaching parameter

Leaching essentially meant dissolution of metallic fluorides (Na_3AlF_6, NaF, CaF_2) and metals like Sodium, Calcium and Aluminum, as they are the most abundant species present in SPL after carbon. (Around 30 % total). Metal fluorides are more ionic than other metal halides. The metals in an oxidation state of +3 or lower for ionic fluorides. The solubility of fluorides has a great variation, but tends to rise with decrease in the charge on the metal[54]

The solubility of metal fluorides increases as the solution becomes strongly acidic (higher pH), since the F^- ion coming as the conjugate base of the weak acid HF is a weak base. So the concentration of F^- ions is reduced by protonation which forms HF, or is attached to other metal complexes. So, from Le Chartelier's principle, the solubility equilibrium of CaF_2 is shifted to the right[50]

In the treatment of SPL, the fluoride solubility involves the formation of AlF_i complexesas they are more stable than the other metal complexes. The dissolution of other complexes of Na and Ca further drives the dissolution equilibria by attaching to itself accessible fluorides to form higher complexes of AlF_3 and AlF_4^-. Also, at 90 °C, the solubility of fluorides maintains a constant, although it can't be generalised for every complex available[47, 48]

Summing up, the solubility of fluorides tend to increase when:

1. Charge on the metal ion decreases. (Na^+, Ca^{2+})
2. The solution becomes strongly acidic (higher pH, or strong acids like HCl, HNO_3)
3. There is presence of stable complexes. (e.g. AlF_i)
4. Temperature of the leaching reaction increases, which drives the solubility equilibrium. in the forward direction. (for endothermic reactions)

e.g. $$CaF_2(s) \rightleftharpoons Ca^{2+}(aq) + 2F^-(aq)$$

$$F^-(aq) + H^+(aq) \rightleftharpoons HF(aq)$$

Overall:

$$CaF_2(s) + 2H^+(aq) \rightleftharpoons Ca^{2+}(aq) + 2HF(aq)$$

5. CONCLUSION

- Initial treatment of SPL with acid/alkali alone was not a better approach for the leaching due to higher requirement. Whereas compared to initial caustic leaching followed by acid leaching leads to more beneficial approach as the requirement of acid was found to be less.
- From the F-test and ANOVA analysis, the significant factors which play a vital role in the calculation of leaching percentage were found. In case of hydrochloric acid, alkali concentration has been found out to be the most significant factor among all the factors, followed by temperature.
- Although acid concentration was not a significant factor, but the effect of a strongly acidic solution (higher pH) drives the solubility equilibria for the compounds present in SPL, and with increase in pH the leaching value tends to increase.
- Water washing of SPL samples after leaching takes a very long time to neutralise the acidic/alkali content after leaching, and therefore requires special attention.
- Optimization of the leaching percentages needs to be done with respect to the optimum S/N Ratio and not just the highest values obtained by experimentation, regarding minimising the cost, having an optimum concentration and temperature, etc.
- A combination of two factors, Alkali concentration (because of its high reactivity with the compounds present in SPL) and temperature (because of its favourability in dissolution equilibria for fluorides) give the best results in leaching.
-

5.1. Future work

- Exploration of treatment of SPL with other types of tribasic acids such as H_3PO_4.
- pH, reaction time and temperature studies for cryolite precipitation, recovery and detailed investigation of the mechanism for the precipitation.
- Use of water washed filtrate as an additive to maintain the cryolite ratio can be studied.
- Developing mathematical models for temperature dependency on fluoride solubility and its fitting with experimental data.
- Pathways of cyanide dissolution during SPL leaching and its factors, to understand its chemistry.
- Prediction of calorific value using the multiple linear regression of ultimate and proximate analysis.

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